Low intensity geoengineering: microbubbles and microspheres

Crazy talk

Geoengineering is crazy. The sheer scale of the aspiration speaks of hubris. Terraforming the planet by pulling down billions of tonnes of carbon dioxide, or pushing millions of tonnes of plastic up into orbit is absurd. The material intensities and costs are ridiculous.

And yet, with no deep cuts in emissions in evidence, with atmospheric CO_2 at <u>390 parts per million</u> and climbing at a rate of about 2 ppm a year, our "safe" working level of 350 ppm is rapidly disappearing in the rear view mirror even as we're pushing the pedal harder to the floor. We do a lot of crazy things.

But what if there was a geoengineering approach that used no materials, almost no energy, works at sea level, with cheap technology we could start deploying at scale *today*?

That's exactly what Russell Seitz at Harvard is proposing. In this post I want to look at his idea of increasing the reflectivity of the oceans with tiny microbubbles, It's a fascinating, low impact concept, though not without some challenges. So I'll also propose a different means to the same end that addresses these issues, and of course has some of its own. Then we can talk about how crazy it all is.

Bright Water

In a remarkable <u>paper</u> published just over a year ago - which I highly recommend reading - Seitz proposed injecting microbubbles of air into seawater, effectively creating an "inverse cloud". Sunlight is scattered back into space from these bubbles. This concept has no material inputs, bubble sparging equipment is cheap and low power, and could be installed on ships already travelling the worlds waterways.

We don't need to <u>launch giant lenses into space</u> or build <u>giant balloon tethered pipelines to the</u> <u>stratosphere</u>. We have a much more down to earth delivery system already in place, in the form of more than 10 000 ships at sea, 1300 working oil rigs and many thousands of retired platforms (3500 in the Gulf of Mexico alone) not to mention islands and suitable coastlines.

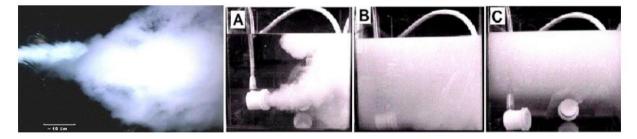


Figure 1. Microbubble sparging [Seitz 2010]. Sparging is stopped at image B and image C is 120 s later. Manufacturer claim for bubble size is ~1 μ m, though the implied rise velocity is consistent with a radius of ~20 μ m, perhaps with smaller bubbles having dissolved.

It's the little bubbles of nothing that make it really something

The appeal of this technique comes from the fact that you only need very small bubbles to scatter light. Leveraging the cube law relationship for volume gives you a *lot* of scattering power if you can make really small bubbles. The air from a single 1 cm bubble, could fill a trillion 1 µm bubbles.

For internal distribution only. This document is confidential to Silverbrook Research Pty. Ltd. If distributed outside the organisation, this document must be covered by a non-disclosure agreement (NDA). Seawater naturally contains up to 1 ppm by volume of air as larger bubbles - in the 10-100 μ m range. Their reflectance can be measured, but is so small as to be irrelevant to the Earth's energy balance. But if this quantity of air were broken down to 1 μ m bubbles, there would be a million more of them, and Seitz estimates the backscattered light would amount to several watts per square metre. That's some serious power.

Light scattering from small spherical particles is calculated using <u>Mie theory</u>, a fairly horrendous piece of mathematical machinery. Seitz reports Mie theory scattering results 1 μ m radius bubbles at various concentrations. At 0.2 ppm of air in water as 1 μ m radius bubbles, the albedo (reflectivity) increase is 1%, equal to the current CO₂ forcing (Figure 2).

This is an astonishing result: global warming is fully offset by 0.2 parts per million of 1 μ m bubbles! Using the IPCC mid-range climate sensitivity of 0.7 K per Wm⁻² the global average temperature would decrease by about 1 degree, more than the 0.74 K warming seen in the 20th century.

The NCAR CAM3.1 climate model was used to look at the effect of 1 ppm of 1 μ m bubbles in a 780 ppm CO₂ scenario - double our current CO₂ level. Under this extravagant CO₂ burden the model nevertheless indicated a *cooling* of 2.7 K [Seitz 2010; Figure 5]. So microbubbles really could be a powerful engineered response to climate change, if we can deploy them.

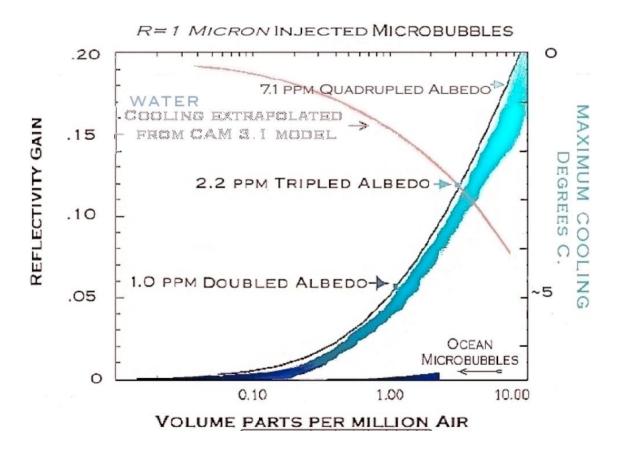


Figure 2. Reflectivity gain from ocean loading of 1 µm radius bubbles [Seitz 2010; Figure 4].

Not so fast

But won't these bubbles just bubble up to the surface and burst? Not the small ones, it turns out. The velocity of a rising bubble is readily calculated (from the <u>Stokes equation</u>), and a one micron radius bubble takes about 5 days to rise a metre. With near-surface mixing they'll be there for a while.

No, the real problem is that the bubbles want to dissolve. The air inside a bubble is at a higher pressure than the water it floats in, because surface tension is trying to pull the surface inwards, and the air is compressed. The pressure increase (given by the <u>Young-LaPlace equation</u>) is greater the smaller the bubble, and can be surprisingly large. For a 1 μ m diameter bubble in seawater, the internal pressure is almost 3 atmospheres greater than the water outside.

At these high pressures the air bubble will rapidly dissolve, even in water that is saturated with air at sea level. Unstabilized 10 μ m bubbles in seawater are observed to dissolve in about 10 seconds. However, as Seitz describes, some seawater bubbles are much more durable, being stabilized by adsorption of natural surfactants and small particles on their surfaces. These materials form incompressible surface films that balance the pull of surface tension, and stabilized bubbles in the micron size range have been <u>observed</u> to last for 20-30 hours.

So the key to the bright water concept is increasing the lifetime of these bubbles by ensuring that they are stabilized somehow. I'll discuss some possible strategies for this below.

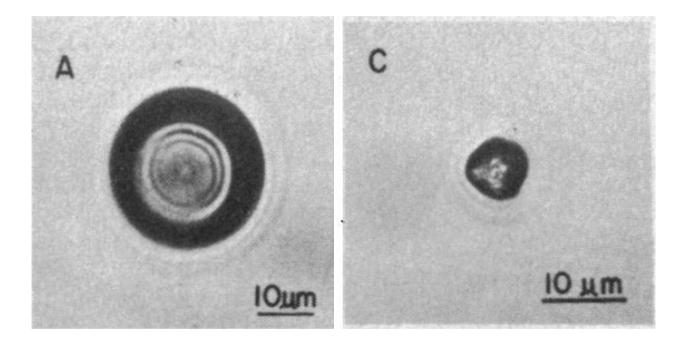


Figure 3. Stable bubble in seawater. The large bubble (left image) shrinks, until adsorbed matter arrests the process, after which the bubble is stable for many hours. [Johnson BD, Cooke RC (1981) *Science 213:209-. 211.*]

I'm forever blowing bubbles

- Doris Day, On Moonlight Bay

Another problem is generation of microbubbles. Making large bubbles is easy. Making small bubbles is hard. To make 1 micron bubbles requires we pressurize air to three atmospheres. We could try to do this by pushing high pressure air through one micron holes. But in practice surface tension effects cause bubbles to stick to the hole and continue to inflate to much larger sizes.

Seitz presents an image of a tank filled with micron scale bubbles generated by a commercial bubbler system (Figure 1). However, I harbour a degree of scepticism for manufacturer claims of bubble sizes especially below 10 μ m, and from the images presented it appears the lower 10 cm has cleared in 120 s, suggesting (from the Stokes equation) that the bubbles are of the order 20 μ m, consistent with my expectations for this kind of technology.

We could instead inject air into a high shear mixer and break large bubbles down to smaller ones, like shaking up a bottle of soapy water. Here we are relying on turbulence to transiently generate 3 atmospheres of pressure throughout the mix. To do this by, say, shaking a drink bottle, you'd need to generate ~150 g acceleration as you shake. Vortex mixers can do this, but it is obviously an energy intensive process. Seitz calculates the energy cost of 1 micron bubble production to be ~1 kW hr m⁻³ of air, a theoretical limit which is unlikely to be obtained in practice.

Seitz estimates that to sustain a bubble concentration of 0.5 ppm bubbles (1 mg m⁻³) in the top 10 m of the ocean would require the injection of 50 million tonne of air a year, if bubble stabilization for 20 hours could be achieved. Ignoring fixed structures and coastline, 10 000 ships would have to disperse about 11 000 m³ of air a day. Each ship would need to generate 11 MW hr a day for bubble generation, requiring 0.5 MW of dedicated generation.

This is obviously a big ask. We can reduce the scale of the task by being more targeted about where and when we generate bubbles - by restricting deployment to the tropics where the sun is nearly overhead, rather than the high latitudes where the sun is low in the sky, and by timing bubble generation for daylight hours only.

Armwrestling thermodynamics

The biggest purely technical problem with the bright water idea is that bubbles are thermodynamically unstable due to their high internal pressure, with quite short lifetimes. An air bubble with 3 atmospheres internal pressure *will* dissolve in water saturated with air at only 1 atmosphere. And the smaller the bubble gets, the faster it dissolves. As observed above, a 10 μ m bubble in seawater <u>lasted</u> 10 seconds. A 1 μ m bubble would presumably last a fraction of a second.

How can we fight this? Well, I can think of a few different ways. We could try to make the bubble surface impermeable to air. Surfactants can improve the barrier properties of surfaces to some kinds of molecular species. Phospholipid bilayers, for instance, are impermeable to water. Unfortunately, they do not present a significant barrier to nitrogen or oxygen molecules, which are soluble in these surfactant layers. I don't believe targeting the barrier properties of bubbles will be successful.

A second approach is to load the bubble surface with a raft of fine particles or proteins, which can support the two dimensional compressive load from surface tension, taking the pressure off the air, rather like a microscopic diving bell. This behaviour is observed in seawater bubbles. The long lived small bubbles reported by Johnson and Cooke were observed to be stabilized by a shell of adsorbed matter (Figure 3).

Could this be a viable strategy for bubble stabilization? I don't think so. Johnson and Cooke report only "some" of the seawater bubbles they observed behaving this way, so we know the yield of stabilized bubbles in natural seawater is small. Stabilizing agents such as surfactants, and surface active proteins - could be added to the water, but the material input would be enormous and capture by low bubble concentrations hopelessly inefficient. And the observed lifetimes are still only about 20 hours.

A third strategy is to apply a bit of thermodynamic jujitsu by adding a trace of an insoluble gas to the air, and use the bubble shrinkage against itself. As the bubble shrinks, the insoluble gas remains, and the partial pressure of the soluble gasses drops faster than the internal pressure rises. The bubble eventually stabilizes at a smaller size.

Hydrogen is not very soluble in water. If 1% hydrogen were added to the air of a 5 μ m bubble, air leakage would be nearly arrested before it got to 1 μ m.

This approach is actually used in medical ultrasound imaging, where stabilized microbubbles are employed as acoustic contrast agents. The insoluble gases favoured are perfluoroalkanes. These are more insoluble than hydrogen, and we have performance data for this system.

The lifetime of these bubbles in blood is short - a half life of 1.3 minutes for one lipid stabilized <u>perfluoroctane bubble product</u>. This does not bode well for bubble geoengineering. These ultrasound contrast agents represent the best that we can do now, under ideal conditions - a small volume, high value cost-no-object pharmaceutical product that can bear the expense of exotic very insoluble gasses and sophisticated lipid encapsulation stabilization strategies - and they still dissolve after a few minutes (Figure 4).

In the end, thermodynamics always wins.

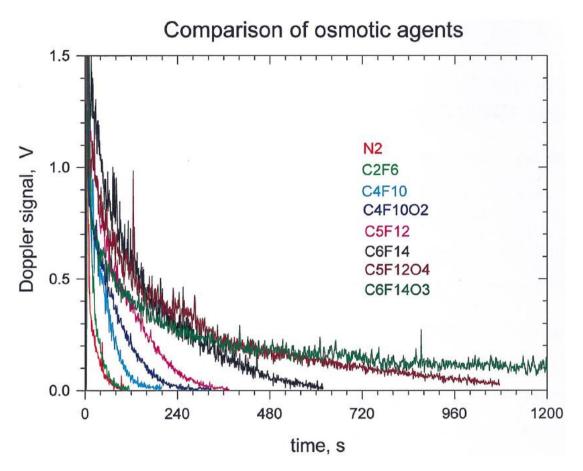


Figure 4. Bubble lifetime for shell stabilized bubbles of various perfluorocarbon gas mixtures at 0.1-0.2 mole fraction, in rabbit bloodstream. [Kabalnov et al., Ultrasound in Med. & Biol., Vol. 24, No. 5, pp. 751-760, 1998.]

Watercolours

Is there another way to look at this? The Achilles heel of the hydrosol approach is the short bubble lifetime. But are there other ways to brighten water? Are there any other micron sized light scattering particles cheaply available in prodigious quantities, which float in water and don't dissolve?

It turns out the answer is yes. Synthetic latex is produced on a huge scale - $\frac{10^{10} \text{ kg in 2005}}{1000 \text{ kg in 2005}}$. A latex is a dispersion of polymer microspheres in water (Figure 5). The particle size is typically around 0.1 - 0.5 µm. The polymer content is high - about 50% by weight. And its cheap - <u>a bit over a dollar per kilo</u>

wet. It looks like a bright white opaque liquid, like wood glue, which is a polyvinylacetate latex. Its a bulk commodity used in adhesives, paper coatings, paint and many other applications.



Figure 5. Beaker of latex, and electron micrograph of latex spheres. The contents of the beaker would treat about 8 ha of ocean at the rate proposed below to offset global warming.

The common polymers are acrylates, polystyrene and its copolymers, PVA, and others. These polymers themselves are inert and non toxic. Whether they present any physical risk to the biota needs to be determined but given the small particle size and low concentration in a milieu already loaded with natural micro- and nanoparticles it seems low risk. The main safety concern in my opinion would be any residual monomers, which are toxic. But these can be eliminated, certainly to the point where these materials can be safely unleashed on the public as paints and glues.

The chief virtues of latex particles over bubbles is they don't dissolve, they don't coalesce, they are durable, and they can be made much smaller. They have a density of just over 1 g cm⁻³ so they sink, but at 0.2 micron the sedimentation velocity is too slow to matter. This presents a different problem - the chief loss mechanism now is not dissolution but loss by convection to deeper waters. Is there some way to keep these particles afloat?

I think there is. Most of these latex polymers, polystyrene, for example, are hydrophobic - they're water repellent. To keep the particles in suspension requires added surfactants, or putting electrically charged groups on the surface. But when diluted with salt water, both these stabilization mechanisms fail. Without stabilization a polystyrene sphere will attach to the water surface. Breaking waves will drive them under, but rising bubbles will scavenge them back to the surface again. This mechanism is well known and extensively studied in the mineral separation process of flotation, where particles of mineral ores are recovered from slurries by attachment to rising bubbles. The natural bubble population from breaking waves could keep even submicron particles concentrated at and near the ocean surface (Figure 6).

The use of latex technology opens other doors for engineering particle properties. For instance, rather than producing a particle composed of a single polymer, its possible to construct a particle with two different polymers in a core-shell morphology, or even hollow particles. Such particles can have much higher scattering power than simple spheres, and are also made in bulk at commodity prices. Indeed, they are used as opacifiers in paint.

We could paint the oceans white.

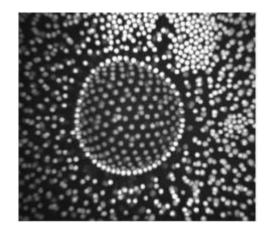


Figure 6. Latex particles adsorbed on the surface of an oil droplet. Similar behaviour would be observed at the air-water interface.

Painting by numbers

Lets run the numbers on this and ask, what would it take to reverse current warming? First we need to know how much light these particles scatter back to space. I used <u>Mie theory</u> to analyse scattering of 500 nm wavelength light (roughly the solar peak) from 0.1 μ m diameter polystyrene spheres, as if the sun were overhead. The back scattering from these very small particles is intense - 42% of overhead light returns to space. And this is just direct scattering. Some of the light that scatters forward will scatter off a second particle, and a third. Multiple scattering will see more than 42% of light returned to space.

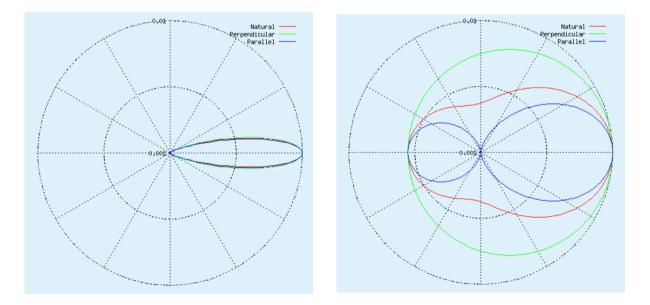


Figure 7. Mie theory light scattering <u>calculation</u> for a 1 μ m air bubble (left) and a 0.1 μ m polystyrene sphere in water (right). The red curve is the angular dependence of scattered intensity for a light ray entering from the left incident upon a particle at the origin. The smaller particle shows much greater direct backscattering. Integration over the rear 180° solid angle gives a direct backscattering of just 0.9% for the bubble, but 41.8% for the particle.

Since these particles attach to the surface, lets consider, for the moment, a monolayer on the water surface. This requires 10^{14} particles per square metre, with a volume of 5.2×10^{-8} m³ per m² (or 5 parts per billion of the top 10 m, for comparison with Seitz' figures). Polystyrene has a density of 1050 kg m⁻³, so that's a mass of 55 mg m⁻². Over 3.16×10^{14} m² of ocean that's 1.7×10^{10} kg polymer.

What would this do to the earth's energy balance? Average insolation (accounting for cloud cover [Jin et al. 2002, cited by Seitz]) is 239 Wm⁻² The monolayer cross sectional area fraction is $\pi/4$. So the energy returned by direct overhead scattering is about 78 W. That's huge compared to the current CO2 forcing of about 2.25 Wm⁻².

Modelling reported by Seitz indicates an increase of ocean albedo of 0.05 translates to an increase of planetary albedo by 0.031 [Seitz 2010; Figure 5]. So I'll assume planetary albedo increase is 60% of the ocean albedo increase, which means we need ocean backscattering of 3.75 Wm⁻². We would only need 4.8% of a monolayer to offset current CO2 forcing (ignoring the contribution from multiple scattering).

4.8% of a whole ocean monolayer is 8.3×10^8 kg of dry polymer, or about 1.7×10^9 kg wet latex. At say \$1.20 per kg, this would cost \$2.0 billion and account for 17% of 2005 global production capacity.

This is, surprisingly, well within reach. \$2.0b to reverse global warming is cheap. Restricting dispersal to the mid latitudes where the greatest effect is achieved, using core-shell latex technology, and properly accounting for multiple scattering would see this cost drop even further. Annual growth in latex production grew organically by 4.5% per annum between 2000-2005. Ramping production by 17% would be completely feasible.

The ongoing cost depends on the residence time of the particles at the ocean surface. Equatorial currents <u>run at about 1 ms⁻¹</u>, which would imply a traversal time of about 1 year for the Pacific ocean. Mid latitude the currents are much slower. The latex particles themselves will degrade in the environment, and there will be losses by association and entrainment in a complex marine environment.

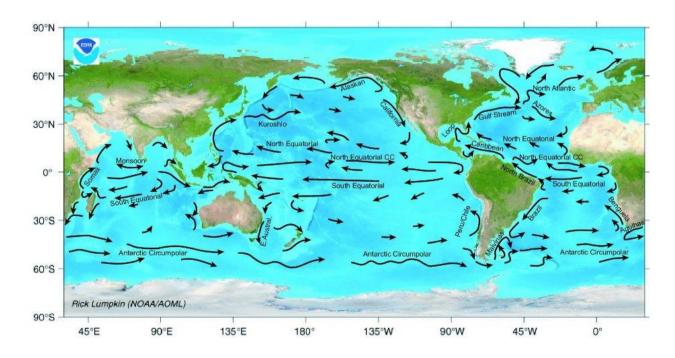


Figure 8. Major ocean surface currents.

But let's provisionally estimate a cost of \$2b per year. This is significantly cheaper than, say, stratospheric sulfur aerosol injection which is estimated at \$25-50b per year, let alone space sunshades. And it doesn't require exotic engineering, enabling R&D, or orbital launches - it uses existing materials at a rate well inside existing production capacity.

Conclusion

So consider this final elaboration of Russell Seitz' bright idea: 0.1 µm diameter latex particles, possibly hollow, or of core-shell morphology, bearing a conventional stabilization system that is inactivated in salt water ensuring that the particles are retained at and near the surface, are produced in bulk using about 17% of existing production capacity and using commercial recipes, and are sprayed onto the sea from tanks aboard ships or crop dusting aircraft, oil rigs, and other structures, in the mid latitudes.

For a cost in the order of a mere \$2b per year we could offset current global warming, subject to the many disclaimers and qualifications discussed above, and many others not mentioned. More limited, local applications, such as the direct cooling of coral reefs as envisaged by Seitz for the microbubble concept, are also possible.

As they say on Top Gear, what could possibly go wrong?